Materials Science and Technology
Solid-state lighting

Red-Emitting Phosphors for White Light-Emitting Diodes

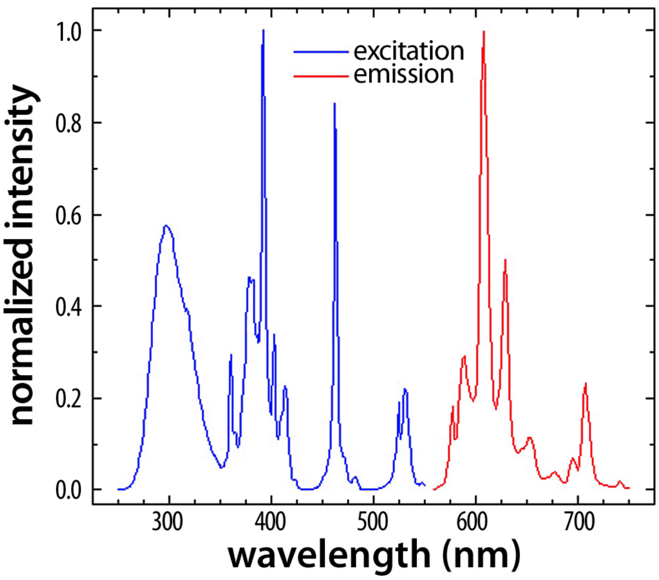

Figure 1: Photoluminescence excitation and emission spectra of Eu^{3+}-doped lutetium tantalate phosphor.

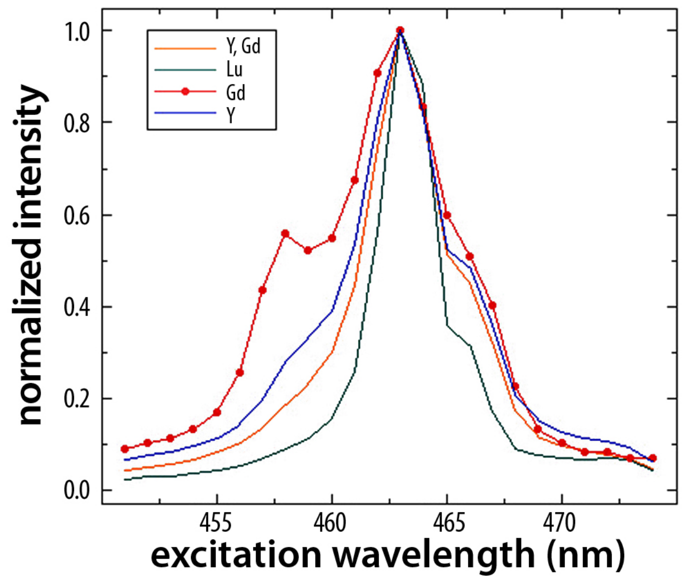

Figure 2: A comparison of the blue excitation peaks of the various rare-earth tantalates shows that the Gd phosphor has a significantly larger excitation bandwidth.

"Warm" white light achievable with new rare-earth structures

Sandia has developed red-emitting phosphors that will help to transform the cold blue of many current light-emitting diodes (LEDs) into the warm white that is preferred for general lighting. This advance could help move solid-state lighting (SSL) into broader applications and market spaces.

The solid-state devices that have been targeted use the nearly monochromatic blue emission from InGaN (indium gallium nitride) LEDs to excite yellow-green emission from Ce^{3+}-doped yttrium aluminum garnet (YAG:Ce) phosphors. These devices produce light in the blue to yellow portion of the visible spectrum, which means that orange or red objects appear dim and colorless under this lighting. Thus to improve their white light quality, these devices require red-emitting phosphors that can be excited by blue LEDs. Thanks to researchers at Sandia, such a family of phosphors is now available.

Most red phosphors are doped with Eu^{2+} ions whose emission is due to parity-allowed 5*d*-4*f* transitions. The 5*d* orbitals are spatially diffuse and their energy levels strongly depend on the local crystal field of the surrounding ions in the lattice. This leads to emission band broadening because of both differences in the atomic environments (inhomogeneous broadening) and phonon coupling (homogeneous broadening). An undesirable consequence of broad emission is deep-red emission, to which the eye is insensitive. The absorption bands are also broad, enabling excitation with near-UV to visible LEDs, but also unwanted absorption of green or yellow emission from other phosphors in the blends. For these reasons, Sandia has focused on narrowband red-emitting phosphors with narrowband blue absorption for SSL applications.

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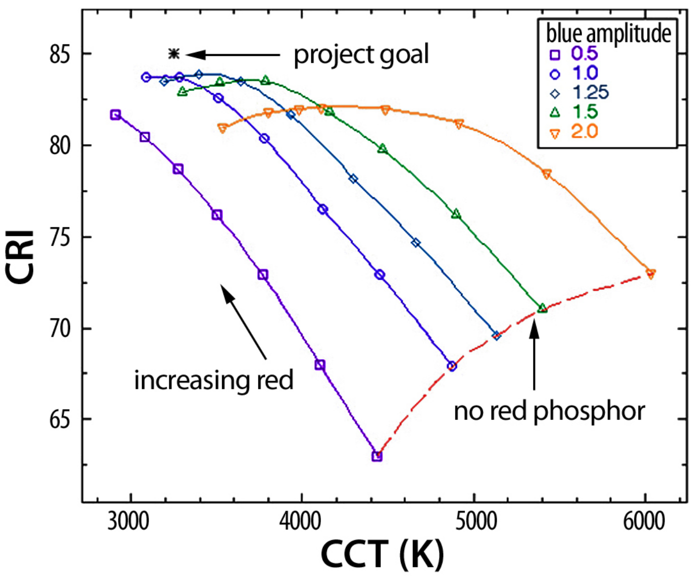

Figure 3: Color quality calculations for luminaires consisting of a 465 nm LED pumping YAG:Ce and Eu^{3+}-doped tantalate blends. The blue amplitude is relative to the amplitude of the YAG:Ce emission (peak to peak). The red dashed line is the locus of points without the red phosphor; decreasing the blue emission reduces the CCT, but at the price of drastically reducing the CRI. At any given blue/YAG:Ce ratio, adding the red emission decreases the CCT while increasing the CRI.

It was discovered here that Eu^{3+} in rare-earth (RE) tantalate phosphors with the pyrochlore structure, K(RE)Ta_2O_7 (RE=Gd, Lu, or Y), can be excited directly with blue LEDs to produce narrowband red emission with efficiencies of nearly 80%, more than three times that obtained from conventional Eu^{3+}-doped phosphors (Reference 1). This narrowband emission is due to parity-forbidden 4*f*-4*f* transitions that are weakly dependent on the crystal field, but are sensitive to the symmetry of the Eu^{3+} site. The pyrochlore structure is highly flexible, offering much greater control over site symmetry than the zircon-type structures of conventional phosphor lattices. The ability to control the site symmetry enables a scientific approach to the development of a useful red phosphor. Thus by altering the oxygen vacancy concentration and the geometry of the Eu^{3+} site, Sandia can tailor the structure in order to decrease the centrosymmetry at each Eu^{3+} location.

These new materials have intense emission at ~610 nm - an ideal wavelength for warm white LEDs (Figure 1). The blue excitation linewidth is important for SSL applications. Figure 2 shows the blue excitation peak for different rare-earth tantalates. The linewidth of the Gd phosphor is nearly twice that of the Lu phosphor. This increased linewidth reduces the need for stringent emission wavelength control of the LEDs, and increases the absorption cross section of the phosphor. Calculations of the color rendering index (CRI) and correlated color "temperature" (CCT) for theoretical blends of blue LED, YAG:Ce, and red tantalate emissions are summarized in Figure 3. Without the red phosphor, the CRI is 73 at a CCT of 6000 K, and the CRI falls to 68 if the YAG emission is increased to give a CCT of 5000 K. Further decreases in the CCT lead to even lower CRIs. By adding the red phosphor, computer simulations indicate that a CRI of 85 at a CCT of 3250 K is achievable, satisfying the criteria of warm white light. The goal is to meet or exceed this color quality in an operating device.

Reference

1. M. Nyman, M.A. Rodriguez, L.E. Shea-Rohwer, J.E. Martin, P. Provencio, "Highly versatile rare-earth tantalate pyrochlore nanophosphors," *J. Am. Chem. Soc.*, ASAP Web release, July 31, 2009.

Sandia National Laboratories

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